

(19) Japanese Patents Office (JP)

(11) Patent Application Number

(43) Publication date: 1989-4-11

Patent Number Hei 1-92209

(12) Patent Notification (A)

| (51) Int.Cl. ⁴ | Identification code | Int. Ref. No. |
|---------------------------|---------------------|---------------|
| C 08 F 212/02 | M J X | 7445-4J |
| B 29 C 47/14 | | 6660-4F |

Investigation request: Not applied

No. of claims: 1

(Total Pages: 14)

(54) Title of the invention

Resin composition for optical purposes.

(21) Application number: Sho 62-248785

(22) Application date: 1987-10-1

(72) Inventor: Niwano Masahiro

Sumitomo Chemical Co. Ltd.

Ehime-ken, Niihama-shi, Sobiraki-cho 5-1

(72) Inventor: Manabe Kenji

Sumitomo Chemical Co. Ltd.

Ehime-ken, Niihama-shi, Sobiraki-cho 5-1

(72) Inventor: Sakakura
Sumitomo Chemical Co. Ltd.
Osaka-fu, Takatsuki-shi, Tsukahara 2-10-1

(71) Applicant(s): Sumitomo Chemical Co. Ltd.
Osaka-fu, Osaka-shi, Higashi-ku, Kitahama 5-15

(74) Representative: Patent Attorney Moriishi Mitsuhiro (and one other person)

1. Title of the invention

Resin composition for optical purposes.

2. Scope of the patent

(1) Resin composition for optical purposes obtained by extrusion molding of a resin material formed from 60 ~ 90 weight % of a polymeric portion mainly consisting of aromatic vinyl monomer and 10 ~ 40 weight % of polyphenylene ether portion.

(2) Resin composition for optical purposes mentioned under (1) of scope of the patent is the optical card substrate.

3. Detailed description of the invention

(Fields of industrial usage)

This invention is concerned with the resin composition for optical purposes.

To put it in detail, this invention is concerned with the resin composition for optical purposes used in optical card substrates, optical disk substrates, all types of lenses etc. and obtained by extrusion molding of specific resins.

(Conventional techniques)

Using the laser optic spot on the optical disk or optical card, the record information that has been engraved on minute unevenness on the disk substrate is detected and by regenerating the image or sound or by changing the optical characteristics of the record engraved on the substrate surface, it is possible to carry out information record regeneration of high density. It is this regeneration of the record that has recently drawn attention.

The disk substrate that is used in such a system of record regeneration requires that it have properties such as transparency, good dimensional stability, small double refraction, be optically homogenous and so on.

With resin material being used as the disk substrate, although large quantities of duplicated substrates can be molded at a low cost, in many cases molecular orientation occurs in the liquefaction as well as cooling process of the resin at the time of molding of the substrate. That double refraction occurs is widely known and this is said to be a fatal defect.

Since it is difficult to avoid molecular orientation during molding, at present only the polymer having methyl methacrylate as the main ingredient is taken as the resin material with low optical anisotropy.

However, since methyl methacrylate is highly hygroscopic, it has defects in that the dimensional stability is inferior, it warps under high humidity and distortion also occurs.

This defect has been mentioned in the Nikkei Electronics journal (07 June 1982 issue; Page 133). For this reason, an aromatic polycarbonate resin that has a low hygroscopic value is used in the compact disk material for audio purposes.

The aromatic polycarbonate resin includes an aromatic ring having a high anisotropy in its main chain and therefore it is difficult to reduce the double refraction of the mold substrate. Although studies on reduction of molecular weight and mold formation conditions are being conducted, due to the fact that the double refractivity originates in that raw material, it is difficult to uniformly stabilize and produce a substrate with a low double refraction. Therefore what needs to be improved is the low double refractivity and production of a substrate through injection molding having a diameter larger than that of the audio compact disk.

For improving the dimensional stability in the polymer having methyl methacrylate as the main constituent, a co-polymer substance comprising methyl

methacrylate and an aromatic vinyl monomer has been proposed in Patent Notifications Sho 57-33446, Sho 57-162135 and Sho 58-88843.

However, in co-polymerization with a vinyl monomer having an aromatic ring, double refraction occurs easily and therefore cannot be put to practical use.

For the disk substrate obtained not only by regeneration of information but also by registration, although a much more superior double refractivity and dimensional stability is required, yet no resin material has been discovered that fully satisfies these requirements.

Even in the optical elements in lenses etc., resin material such as methacrylate resins and others have been used until now but what is being demanded is a resin material having a much lower double refraction, excellent heat resistance, mechanical strength and dimensional stability.

In US Patent Notification 4,373,065, it has been reported that the resin material has an exactly opposite optical anisotropy. Here, two types of polymer that melt completely are mixed in a composition that exactly negates that optical anisotropy and it results in an optically recorded element which is formed from an optically isotropic resin in which the double refractivity becomes practically zero.

In the said Patent Notification, it has also been mentioned that in the system of using polyphenylene ether and polystyrene as the polymers having an exactly opposite

optical anisotropy, even if stress is applied on the film that is made from the composition of the mixture that exactly negates that optical anisotropy, double refraction does occur. In other words, when a polymer compound in a solid state is stretched, it was seen that double refraction did not occur.

(The problems that this invention seeks to solve)

The US Patent Notification 4,373,065 mentioned above does not say as to how the double refractivity of the optical material becomes remarkably small when the optical material for the optical disk substrate or optical card substrate is produced either through injection molding or extrusion molding using the polymer compound as the base material.

The optical anisotropy exists in the solid state. When two types of polymer that melt completely are mixed in a composition, the optical anisotropy in that solid state was seen to exactly negate the mixture composition. When the substrate was molded through extrusion molding, it was found that the double refraction of the mold obtained was not necessarily small.

In other words, when an optical raw material for the optical card substrate is to be prepared through extrusion molding using the polymer compound as the raw material, the optical material having a small double refraction cannot be obtained merely by singularly

forming the solid state optical anisotropy for individual polymers to the composition in which it has been thought of.

This invention has taken note of these problems and provides for a resin composition for optical purposes where the double refraction is low even when extrusion molding is adopted, the heat resistance is high, the mechanical strength balance is good and the dimensional stability is excellent.

(Procedure for solving these problems)

This invention is concerned with the resin composition for optical purposes obtained by extrusion molding of a resin material comprising 60 ~ 90 weight % of a polymeric portion mainly consisting of aromatic vinyl monomer and 10 ~ 40 weight % of polyphenylene ether portion.

The resin material in the resin composition used for optical purposes in this invention results from a mixture of a polymer compound in which an aromatic vinyl monomer unit is the main ingredient and polyphenylene ether or its block co-polymer or graft co-polymer resulting from the polymer portion of both the compounds or else it results from a mixture of all of these.

The polymer having the aromatic vinyl monomer unit as the main ingredient mentioned in this invention is the aromatic vinyl monomer-independent polymer and also it is the co-polymer which has more than 50 weight % of an aromatic vinyl monomer unit. Styrene, α -methyl styrene, m-methyl styrene, p-methyl styrene, o-chlorostyrene, m-

chlorostyrene, p-chlorostyrene, m-bromostyrene, p-bromostyrene etc. are examples of aromatic vinyl monomers, out of which styrene is the most desirable.

Examples of monomers that co-polymerize with aromatic vinyl monomers are unsaturated nitril class compounds like acrylonitril and methacrylonitril; alkyl ester methacrylate class compounds like methyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, cyclohexyl methacrylate; alkyl acrylate class compounds like methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate etc. There are also other compounds like methacrylic acid, acrylic acid, maleic anhydride, citraconic anhydride, N-methyl maleimide, N-phenyl maleimide etc. that can be used

The polymers that co-polymerize with these compounds can each be used either independently or as a mixture. It is better if the combination and regulation of the usage ratio of the co-polymer from the aromatic vinyl monomer as well as the resin material resulting from the aromatic vinyl monomer and polyphenylene ether are carried out without any hindrance.

It is desirable that the proportion of the aromatic vinyl monomer in the monomer mixture be more than 50 weight %. If the aromatic vinyl monomer is less than 50 weight % then the hygroscopic level of the resin becomes high, which is not desirable.

Further, the melt fluidity (MFR)_{ps} of the polymer that has the aromatic vinyl monomer unit as the main ingredient, conforms to ASTM D1238. The melt flow rate at 230°C and 3.8 kg. load is given as g/10 min.

This value is in the range of 0.5 ~ 200 but the desirable range is 2 ~ 100.

If it exceeds 200, then the mechanical strength declines, which is not desirable and if it is less than 0.5 then reduction of double refraction becomes difficult, which is also not desirable.

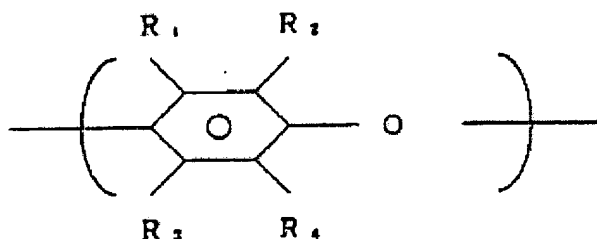
The method of production of the polymer that has the aromatic vinyl monomer unit as the main ingredient could be any of the methods that use a radical initiator such as block polymerization, suspension polymerization, emulsion polymerization or solvent polymerization. However keeping in mind the objective of obtaining a polymer with good productivity and having fewer impurities mixed in, block polymerization or suspension polymerization are desirable.

Peroxides like lauryl peroxide, benzoyl peroxide, di-tertiarybutyl peroxide, di-cumyl peroxide and azo compounds like 2,2'-azobis-isobutyronitrile, 1,1'-azobis (1-cyclohexane carbonylnitrile) can be used as radical initiators.

To control the molecular weight, chain-transfer agents such as tert-butyl, n-butyl, n-octyl, n-dodecyl and tert-dodecyl mercaptan may be added.

Polymerization is generally carried out in the temperature range of 50 ~ 150°C.

The polyphenylene ether mentioned in this invention is represented in the general form and is a polymer that has repeating units.



(Here, R₁, R₂, R₃, R₄ stands for a hydrogen, halogen or a hydrogen carbide group.)

The said polyphenylene ether is a polymer that has been polymerized from a phenol class monomer through oxide coupling. Polyphenylene ether is a compound that can be easily manufactured through known methods (Patent Notifications Sho 36-18692 and Sho 47-36518) using a copper group or manganese group catalyst.

Definite examples of polyphenylene ethers are compounds such as poly(2,6-dimethyl-1,4-phenylene)ether, poly(2-methyl-6-ethyl-1,4-phenylene)ether, poly(2-methyl-6-propyl-1,4-phenylene)ether, poly(2,6-dipropyl-1,4-phenylene)ether, poly(2-methyl-6-bromo-1,4-phenylene)ether etc., out of which poly(2,6-dimethyl-1,4-phenylene)ether is preferred.

This polyphenylene ether is generally used as an engineering plastic but a compound with a much lower molecular weight is suitable.

In other words, the average molecular weight of polyphenylene ether is represented in the limiting viscosity of the polymer (η)_{PPE} (measurement and computation at 25°C in chloroform solution). Polyphenylene ether with a molecular weight of 0.1 ~ 1.0 can be used; however, the desired weight is 0.3 ~ 0.5.

If the molecular weight is less than 0.3, then the mechanical strength of the resin composition used for optical purposes becomes small.

Also a molecular weight of less than 0.5 is desirable in order to minimize the double refraction as well as double refraction for specifically inclined incident light rays.

It is thought that this is because the alleviation speed in the orientation of the polymer portion that has the aromatic vinyl monomer as the main ingredient and the polyphenylene ether respectively and/or the alleviation speed in the orientation of the polymer differ when the optical element is produced through extrusion molding.

The ratio of the polymer portion having the aromatic vinyl monomer as the main ingredient and the polyphenylene ether portion is 60 ~ 90 weight % of the former, preferably 65 ~ 85 weight %, to 40 ~ 10 weight % of the latter, preferably 35 ~ 15 weight %.

If the polyphenylene ether portion is less than 10 weight % or exceeds 40 weight %, then the double refraction of the resin compound for optical purposes obtained

through extrusion molding, does not get sufficiently lowered. Besides this, the heat resistance is also not sufficient.

To obtain the resin material for the resin compound for optical purposes by mixing a polymer that has the aromatic vinyl monomer as the main ingredient and polyphenylene ether, methods such as fusion mixing or solution mixing are suitable.

Fusion mixing is carried out at a temperature higher than the fusion temperature of the polyphenylene ether and using mixing machines such as an extruder, Banbury mixer, kneader-blender, heat rolls etc. under high shearing.

The degree of fusion should be to the extent that both the polymers are mutually dispersed and mixed up to approx $1\ \mu$ and further on they are mixed up to the molecular level.

Whether the mixture state has reached the molecular level or not can be judged easily when the glass transition temperature of the mixture becomes constant.

In order to obtain a very satisfactory mixture state, methods such as raising the mixing temperature, prolonging the mixing time and raising the shearing power are adopted.

Further in fusion mixing, to make the mixing easy by lowering the mixing temperature of both the polymers, small quantities of an organic solvent can be used as a plasticizer.

As for the organic solvent, the one that is used in the solvent mixing method mentioned in later pages can be used here. After the mixing process is completed, it is better if the used organic solvent is removed through evaporation.

In solvent mixing, both the polymers are dissolved in the organic solvent and at least 1 weight % of the solvent is produced. After getting a uniform mixture through stirring, the organic solvent is removed through evaporation; alternatively, it is also possible to add a poor solvent in both the polymers to the uniform mixture and then precipitate the polymers that have been mixed.

The suitable organic solvents are chloroform, methylene chloride, ethylene chloride, toluene, benzene, chlorobenzene etc. Poor solvents are compounds such as methanol, ethanol, propyl alcohol, n-hexane, n-pentane etc.

The block co-polymer or graft co-polymer formed from the polymer portion having an aromatic vinyl monomer unit as the main ingredient and the polyphenylene ether portion is obtained by polymerizing the polymer on one hand with the monomer on the other hand.

In specific terms, as per the methods mentioned in Patent Notifications Sho 42-22069, Sho 47-1210, Sho 47-47862 and Sho 52-38596, the monomer that has the aromatic vinyl monomer as the main ingredient is polymerized in the presence of polyphenylene ether. Alternatively, the graft polymer or block co-polymer can be produced by polymerizing a phenol class monomer through oxide coupling in the presence of a polymer that has an aromatic vinyl monomer unit as the main ingredient.

The polymer that has an aromatic vinyl monomer unit as the main ingredient (mentioned above) or polyphenylene ether may be mixed into this graft polymer or block co-polymer.

The extrusion molding mentioned in this invention is a common type of method for manufacturing thermo plastic resin sheets and is a molding method that uses a sheet extrusion-molding device.

The said extrusion-molding device is fabricated from a normal extruder and sheet die, cooling roll, transfer device as well as from such incidental devices.

Usually it is possible to mold a sheet, which is 1 mm thin to a sheet having close to 10 mm thickness.

It is desirable that the resin temperature at the time of molding is above 230°C and below 350°C; however a temperature of 240°C to 300°C would be more desirable.

The resin temperature mentioned here is the temperature of the fusion resin at the die lip.

If the resin temperature is below 230°C, then the double refraction of the optical card substrate obtained will be more than 20 nm and would therefore not be suitable for optical card substrates or optical disk substrates. And again, if the resin temperature exceeds 350°C, then defects such as resin decomposition, coloration, fish eye, thickness, unevenness, die lines etc. develop easily and the pit error of the optical card substrate increases remarkably.

The surface temperature of the cooling roll is between 50°C to 200°C but the preferred temperature is in the range of 80°C to 150°C.

If the surface temperature becomes too low, then the adhesiveness of the cooling roll for the extrusion sheet declines and the surface roughness and level become bad. If the surface temperature becomes very high, then the roll separation becomes bad and the release pattern is generated in the extrusion sheet, which is not desirable.

Since the surface state of the cooling roll gets transcribed on the surface of the contact extrusion sheet, a mirror surface finish of below 0.3 S is desirable.

The sheet that has been obtained through extrusion molding is processed to the prescribed shape through thermal fusing and mechanical decomposition.

Even within the optical card substrate, optical disk substrate or lens, the temperature of the surface of the extrusion sheet is raised to more than that of the glass

transition temperature and then stamped. This is a manufacturing method whereby minute unevenness is provided on the surface just as is done in the Fresnel lens.

When the optical card substrate or optical disk substrate is considered within the said resin mold, semiconductor laser optics comes to mind.

Consequently, it is desirable that the light transmission rate for an 800 nm wavelength be more than 75% for the material having 1.2 mm thickness and more than 85% for the material having 0.4 mm thickness.

(Application examples)

This invention is explained below in detail through application examples. The invention however, is not restricted only to these examples.

Both the division and percentage in these Application Examples are by weight.

The properties of the substances shown in the Application Examples have been measured through the methods given below.

- *Double refraction:* The refraction was measured using a polarized microscope at 546 nm by the Senarmont Compensator method.
- *Suction rate:* The equilibrium suction rate of 60°C distilled water was measured based on ASTM D-570..
- *Light rays transmission rate:* The transmission rate for a sample thickness of 1.2 mm was measured through an auto-spectrophotometer (Hitachi-make; Model 330) at 800 nm.
- *Viscosity limit of the polymer:* The viscosity limit of the polymer was measured in a chloroform solvent at 25°C using the Ubbelohde viscometer.

- *Melt flow rate:* The melt flow rate was measured under a temperature of 230°C and 3.8 kg load and conforming to ASTM D-1238.
- Kneading and pelleting were carried out through a bi-axial extruder. (Japan Seiko Co. Ltd-make; Model TEX30-30BW-2V).
- The extrusion-molding machine used was a Tanabe Plastic Machinery Co.-make 30 mm Ø sheet extrusion device (Aperture of the extruder: 30 mm Ø, Diameter: 400 mm wide, Rib gap: 0.5 mm, Cooling roll: 250 mm Ø aperture, Surface viscosity: 0.3 S).
- The injection-molding machine was a Toshiba Machinery Co.-make IS-25 (25 ton). A metal pattern having a film gate with a gap of 0.2 mm and cavity of 0.4 mm x 54 mm x 85.5 mm was used.

Application Examples 1 ~ 3, Comparative Examples 1 ~ 3

In accordance with the method given in Application Example 2, No.9 in Patent Notification Sho 47-36518, 2, 6-xyleneol was polymerized using manganese chloride and ethanolamine as a catalyst from which poly(2, 6-dimethyl-1, 4-phenylene)ether having a viscosity limit of 0.40 (in chloroform at 25°) was formed.

This polyphenylene ether and polystyrene resin (Sumitomo Chemical Industries make Esbrite[®] 4-62, MFR 24) was mixed and compounded as per the proportion shown in Table 1. This was kneaded and granulated using a bi-axial extruder and then pelleting was done.

The said pellet was supplied to an extrusion device having a cylinder temperature of 270°C, die temperature of 260°C and cooling roll temperature of 120°C and a sheet having a thickness of 0.4 mm and a width of 380 mm was obtained.

The results of the evaluation of the properties of the sheet obtained are given in Table 1.

Table 1

| | | Application Example 1 | Application Example 2 | Application Example 3 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 |
|------------------------------------|---------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Composition (%) | Polyphenylene ether | 2 0 | 3 0 | 4 0 | 5 | 5 0 | 7 0 |
| | Polystyrene | 8 0 | 7 0 | 6 0 | 9 5 | 5 0 | 3 0 |
| Light transmission rate (%) | | 9 1 | 9 0 | 8 8 | 9 3 | 8 6 | 7 0 |
| Double refraction (nm) | | - 8 | + 7 | + 10.0 | + 4 0 | + 2 5 | + 4 0 |
| Suction rate (%) | | 0. 1 | 0. 1 | 0. 1 | 0. 1 | 0. 15 | 0. 2 |

Comparative Example 4

The poly(2, 6-dimethyl-1, 4-phenylene)ether, which was earlier used in Application Example 1, was used here independently and extrusion molding was carried out.

The molding could not be carried out under identical conditions as that in Application Example 1. The cylinder temperature and the die temperature were raised to 300°C but even then a good sheet could not be extruded.

Comparative Example 5

The polystyrene resin that was used in Application Example 1 was used independently and molding was carried out under identical conditions as that in Application Example 1.

The absolute value of the double refraction was more than 50 nm and the distribution unevenness was also large.

Comparative Example 6

Using bisphenol A as the base material and methylene chloride as the solvent, phosgene was blown according to the usual method and interfacial condensation was carried out. A polycarbonate resin having an average molecular weight of approx. 25, 000 was obtained.

Here, t-butyl phenol was used to regulate the molecular weight.

The powder resin obtained was then granulated through an extruder and extrusion molding was carried out under similar conditions as that in Application Example 1.

However the double refraction of the sheet obtained was on average 160 nm and deviation too was ± 30 nm large.

Comparative Example 7 ~ 9

The polyphenylene ether and polystyrene resin used in Application Example 1 were mixed and compounded according to the proportion shown in Table 2. This was kneaded and granulated using a bi-axial extruder and then pelleting was done.

The said pellet was subjected to injection molding under a cylinder temperature of 310°C, metal pattern temperature of 105°C and having a film gate with a gap of 0.2 mm. Subsequently, an optical card substrate having a thickness of 0.4 mm, width of 54 mm and length of 85.5 mm was obtained.

The properties of the card substrate obtained are shown in Table 2.

Here, the double refraction value is that which has been measured at the center of the card substrate.

Table 2

| | | Comparative Example 7 | Comparative Example 8 | Comparative Example 9 |
|------------------------------------|------------------------|----------------------------------|----------------------------------|----------------------------------|
| Composition (%) | Polyphenylene ether | 20 | 25 | 30 |
| | Polystyrene | 80 | 75 | 70 |
| Light transmission rate (%) | | 91 | 90 | 88 |
| Double refraction (nm) | | - 55 | - 31 | - 20 |
| Suction rate (%) | | 0.1 | 0.1 | 0.1 |

Effect of this invention

The sheet molding in the resin composition for optical purposes given in this invention has a much higher productivity. Even in the extrusion molding method where it is easy for the double refraction to occur, it is possible to have a low double refraction.

Since the heat resistance and mechanical strength in the resin composition is much superior than what it was before, it is suitable for use in the substrate, lens etc. of optical card substrates and optical disk substrates when light rays having a specific wavelength are used. Therefore it can be said that it is suitable for use in optical card substrates and optical disk substrates.